December 23, 2003

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Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period from Nov. 03, 2003 to Dec. 03, 2003, under the subject subcontract. The report highlights results from Task 1 (CdTe Solar Cells.)

UNDERSTANDING THE UNIVERSITY OF TOLEDO'S ANILINE-BASED CdTe SURFACE TREATMENT

At the previous team meeting (NREL, July 10-11 2003), Victor Karpov presented recent work from the University of Toledo (UT) investigating the treatment of CdTe substrates under illumination in either red wine or in aqueous aniline solutions. Following treatment, completed devices exhibited substantial improvement in performance compared to non-treated devices or devices that were treated in the dark [1]. This effect was proposed to be the result of neutralization of micro-nonuniformities, possibly by adsorption of charged polyaniline colloids. IEC offered to assist UT in understanding of the solution and surface chemistry that may be involved. The following is a brief report of our preliminary findings.

Unless otherwise stated, all solutions were freshly prepared and consisted of 0.2 M aniline, 0.1 M p-toluenesulfonic acid (p-TSA) and 1 M NaCl. Treatments were generally carried out for 1h. The pH of the standard bath is ~6.2, and did not change following treatment of CdTe. Samples consisted of $CdCl_2$-treated ~5μm thick IEC vapor transport deposited CdTe on chemical solution deposited CdS. The samples were illuminated with a 100W bulb. Solution temperature was not controlled, however, this did not rise above

mid-30's C during illumination. Samples were generally illuminated through the glass side of the CdTe substrate. Dark treatments were carried out by completely wrapping the beaker in aluminum foil.
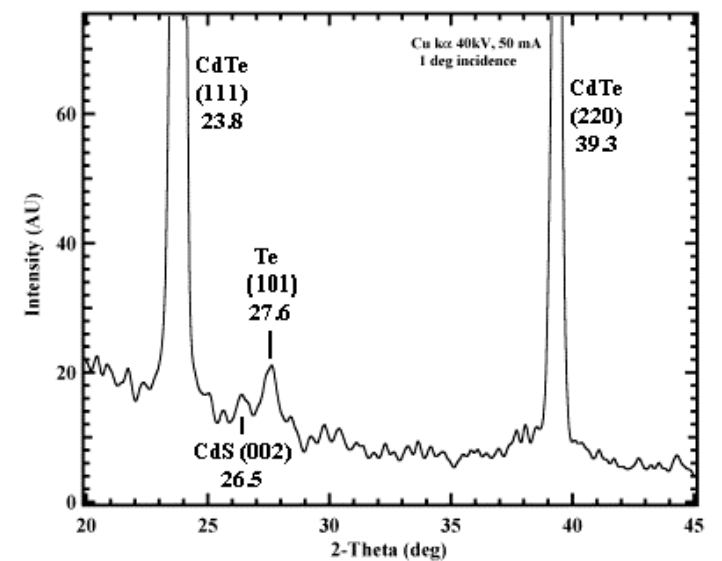
SAMPLES UNDER ILLUMINATION

Following some treatments the CdTe surface changed color to light gray, though not always uniformly. This color change was observed for pieces where Te-rich surface were formed during treatment (see below).

Variable angle spectroscopic ellipsometry (VASE) and glancing incidence x-ray diffraction (GIXRD) both confirm the presence of crystalline elemental tellurium, following successful treatments, on the CdTe surface of the samples that received illumination. Figure 1 shows the VASE ε_2 vs. photon energy spectra of a CdTe/CdS sample before and after treatment in a standard bath. Before treatment the spectrum contains two peaks due to CdTe, however, after etching the spectrum now contains a single peak ~2 eV, due to Te [2]. We have not yet modeled the data to estimate thicknesses, though ellipsometry shows that a reasonable amount of Te is presence as the CdTe peaks are not discernable. Figure 2 shows the GIXRD pattern, obtained at 1 incidence, of a CdTe/CdS sample following illuminated treatment in a standard bath. The Te(101) peak is present at 27.6 , while the peak at 26.5 can be assigned to CdS exposed at the edge of the piece.
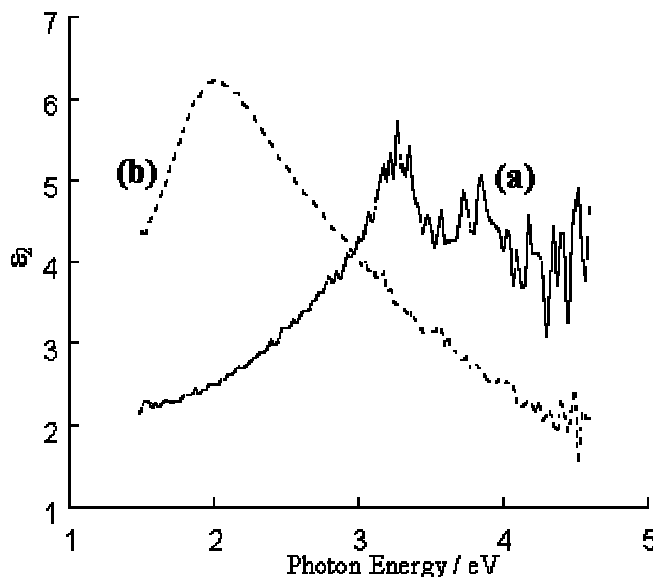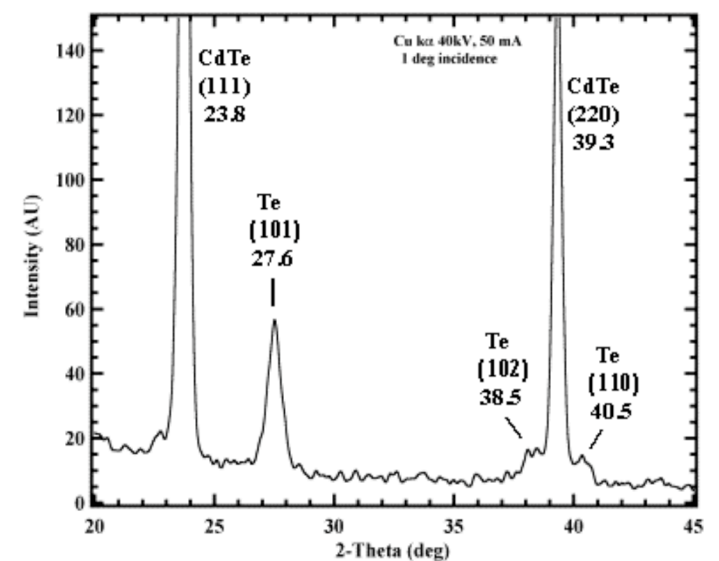

Figure 1 – VASE spectra of CdTe sample VT89-42a (a) before and (b) following 1h treatment in an aniline bath, containing 1M NaCl electrolyte, under illumination through glass.

Figure 2 – GIXRD, at 1 incidence, of CdTe (VT89-42a) following 1h treatment in an aniline bath, containing 1M NaCl electrolyte, under illumination through glass.

Similar results were also obtained when the CdTe film was directly illuminated. We note that significant stray light was present in the beaker and that the CdTe illuminated piece probably also received significant light through the glass side. One piece was illuminated perpendicular to the lamp – again a degree of illumination is expected because of reflection, however, a lesser amount of Te was formed.

Long treatments resulted in, according the GIXRD, a much greater amount of generated surface Te. Figure 3 shows the GIXRD pattern of a CdTe/CdS sample that had received 5.5h illumination in the standard bath, and confirms the presence of more Te on the surface than observed for 1h treatments (Figure 2). A dark organic film was also visible on the surface. VASE spectra of this piece were very similar in intensity to the spectrum shown in Figure 1, despite a greater amount of Te being generated. A stronger Te peak is expected, however, the presence of the organic film, most likely polyaniline will result in a decrease in the VASE spectral intensity.

Figure 3 – GIXRD, at 1 incidence, of CdTe (VT89-11c) following 5.5h treatment in an aniline bath, containing 1M NaCl electrolyte, under illumination through glass.

Some initial treatments were carried out under ambient laboratory lighting at room temperature. After a 1 hr treatment, no visible change could be seen on the CdTe surface. Ellipsometry shows some subtle changes, consisting of a slight decrease in the intensity of CdTe peaks and the formation of a weak peak around 2.5-3 eV. It is not clear what these changes are due to. The new peak, due to its high energy, is unlikely to originate from Te. Preliminary modeling of the data suggested the presence of an ~80A organic film on the CdTe surface. This, however, has not been confirmed at this point.

Ellipsometry confirmed that no changes occurred on the CdTe surface after treatment in the dark. This indicates that the system is very sensitive to the presence of light.

EFFECT OF TEMPERATURE

As solution temperature does rise during illumination, the effect of temperature on the reaction was investigated. A piece was treated in a standard bath in the dark and held at 40-50 C for 1h. No effects were noted on the surface of the CdTe. Ellipsometry showed very little change to the surface, possibly some dissolution of oxides, but no Te was formed. However, following treatment in a standard bath at ~90 C in the dark, a significant surface reaction occurred. The surface became uniformly light gray, and a thin dark organic film was visible on the surface. Ellipsometry confirmed the formation of significant surface Te, however, the spectral intensity was very low due to the organic film.

A similar effect of temperature has been previously reported for a bath containing aqueous NH_3, NH_4Cl, and citrate ions plus Ni^{2+} and Al^{3+} sources [3]. This bath was used to

deposit NiTe$_2$ contacts on CdTe at ~90 C. As the reaction progressed, the surface became light gray within 10 min of immersion, due to the formation of a Te-rich surface. The reaction would only occur at high temperature and only with NH$_3$, NH$_4$Cl and citrate ions all present.

SOLUTION CONCENTRATION EFFECTS

Experiments were carried out under illumination with using baths containing varying concentrations of aniline. Baths containing 0.4 M aniline were cloudy, due to the low solubility of aniline at this pH. However, the ellipsometry of the treated CdTe was very similar to those obtained from standard baths. Treatment in baths of 0.1 M aniline, showed practically no reaction over the 1hr treatment time. Experiments carried out in the absence of aniline showed no surface color change and only subtle changes to the surface were observed with VASE, similar to those with ambient room light during treatment. These observations confirm the direct involvement of aniline in the reaction to form Te.

Increasing the concentration of *p*-TSA to 0.06 M (pH = 5.8) also resulted in no surface reaction on the CdTe. This is consistent with the known chemistry of aniline [4], where the protonated form of aniline has been found to be more difficult to oxidize and also confirms that the formation of Te is directly related to the reactivity of aniline.

EFFECT OF ELECTROLYTE

Varying the concentration of the NaCl electrolyte was also found to have a significant effect on the CdTe surface reaction. Illuminating in the presence of only 0.5 M NaCl, the reaction was significantly slowed and only very small amount of Te was formed on the CdTe surface. In baths where NaCl was not added, no surface reaction occurred. Doubling the NaCl concentration resulted in a significant surface reaction as well as the formation of a visible organic film on the CdTe surface.

We also tested the effect of substituting NaCl with other electrolytes, including KCl, NaBr and NaI. It has been previously shown that the choice of electrolyte can have an effect of the oxidation chemistry of aniline [4]. Using 1M NaBr as the electrolyte, no surface reaction was observed under illumination. With 1M KCl as the electrolyte, a similar reaction to 1M NaCl was observed. From these results, it appears that the presence of Cl$^-$ ions is critical for the reaction to occur. However, using 1M NaI as the electrolyte led to a significant surface reaction on the CdTe. Ellipsometry indicates that Te is formed, however, significant CdTe peaks, which are normally not observable for 'NaCl-treated' samples, are still present in the spectra, indicating less surface Te was formed. The overall intensity of the NaI spectra was similar to the NaCl spectra, despite less Te being formed. This may be due to less adsorbed polyaniline being formed on the CdTe surface due to the slower reactivity of the NaI baths.

EFFECT OF CdTe CdCl $_2$ -TREATMENT

The effect of CdCl$_2$ treatments on the reactivity of CdTe towards the aniline bath was investigated. Non-CdCl$_2$ treated pieces still show a color change after treatment, due to the presence of Te, confirmed by VASE. The rate of the reaction on non-CdCl$_2$ CdTe may be a slower, but this may be due to morphological effects or lower conductivity of non-CdCl$_2$ treated pieces.

OTHER COMMENTS

The non-uniformity of the surface reaction maybe due to undissolved aniline droplets attaching to the surface on immersion of the sample and blocking the surface reaction. When under illumination, the surface reaction does not appear to occur near the clip. This may be due to effects of shadowing by the clip. This was confirmed by carrying out a treatment with a sample which had a small pattern of tape placed on the glass. After a 1.5h treatment in the standard NaCl bath, a pattern of unreacted CdTe, coinciding with the tape pattern, was observed on the CdTe surface. This confirms that, during illumination, CdTe will react only over areas of the device that have received direct illumination and the photo-catalytic nature of the reaction.

We can conclude that a successful illuminated or thermal treatment results in the formation of a crystalline Te-rich surface layer on the CdTe surface. A successful treatment requires the presence of aniline, Cl$^-$ electrolyte, careful control of pH and excitation by illumination or heating. Long or faster, e.g. high temperature or higher Cl$^-$ electrolyte concentration, treatments also result in the deposition of an organic film on the surface. Analysis of the organic films has yet to be carried out. As such, we are currently awaiting AFM results for a number of the samples described here.

The presence of a Te-rich back surface will certainly result in improvement of devices contacted with a Cu-based back contact, and will account for performance improvement observed by UT between untreated and treated cells. The effect of adsorbed polyaniline on device performance is not clear. However, polyaniline is a well known conducting polymer and its presence could possibly enhance the conductivity of the CdTe surface/back contact.

At this point, we are not sure of the chemical mechanisms that may be occurring. One possibility is that photo-polymerization is occurring in solution, and maybe a by-product of that is etching the surface. Similarly, a photo-/thermo-catalytic degradation of aniline, involving the CdTe surface and generates surface Te, maybe occurring.

EFFECTS OF TREATMENTS ON CdTe FILM CONDUCTIVITY

One pathway to increasing V$_{OC}$ in CdTe/CdS devices beyond 850 mV is to increase the p-type conductivity of the CdTe film, which may reduce the recombination current at the CdTe-CdS junction. The lack of understanding of how deposition conditions and post-

deposition treatments affect electronic properties of the CdTe film is an obstacle to this goal. The improved device performance that is obtained after anneals and thermal treatments in $CdCl_2$ and air are not entirely explained by reduced interfacial strain or by extrinsic doping by Cl or O species or by grain growth, or by grain boundary passivation. In fact, extrinsic doping of CdTe single crystals has been shown to be an inefficient process that depends on the Cd-Te equilibrium. In films deposited by condensation, from stoichiometric vapor, at relatively high substrate temperature, the equilibrium will be shifted towards slight Te excess as a result of higher Cd partial pressure. This is the first step towards p-type conduction. It has been shown in theoretical works [5] and by experiment [6] that p-type conduction is facilitated by formation of complexes with Cd vacancies.

Heating CdTe films in chemical environments that remove lattice-bound Cd shifts the equilibrium, creating Cd vacancies at the grain surfaces. These can redistribute throughout the film given sufficient time at temperature. To examine the electrical effects of different treatments on CdTe films, we measured cross-grain dark and light conductivity and thermovoltage on PVD CdTe films on borosilicate glass. For temperature dependent conductivity measurements, the four-contact current-voltage method with high-aspect ratio contacts was employed in light and dark. For thermovoltage measurements, a steel hot probe at 200°C was applied to the film surface at a distance 1 cm from a room temperature probe.

The first sample set, examining HTA and Te vapor treatments, utilized Au and Te/Cu/Au contacts. Negligible differences were found between the different contacts. In subsequent samples, Cu/Au contacts were used, consisting of 10 nm Cu and 50 nm Au. IEC's co-planar contact mask was used, having 0.05cm spacing. Samples were measured as a function of temperature (220 to 370 K) in the dark and then at 300K in the light. The voltage range was selected to give measurable currents: ±10, 20, 40 V. Table 1 shows dark and light conductivity results measured at 300K and the dark conductivity activation energy for the following post-deposition treatments: none; Ar @550°C for 60 min (standard HTA); or Te vapor @550°C for 60 minutes. The first group received no $CdCl_2$ treatment, while the second group had a vapor $CdCl_2$ treatment (410°C, for 20 minutes in Ar/O_2).

Table 1. Conductivity results for CdTe/glass samples. The first set of samples did not receive a $CdCl_2$ treatment while the second set did.

Piece	Treatment	Contact	Thermo- Voltage (mV)	σ_D (S/cm)	σ_L (S/cm)	Ratio L/D	E_a (eV)
32a	None	Au	-3	4E-9	8E-7	200	0.64
11a	Ar, 550C, 60' (HTA)	Au	+2	7E-7	2E-4	280	n/a
21d	Te, 550C, 60'	Au	+10	6E-7	9E-6	15	0.22
21c	None	Te/Cu/Au	-1	9E-9	1E-6	110	0.37
32b	Ar, 550C, 60' (HTA)	Te/Cu/Au	+4	1E-7	9E-5	900	0.49
11b	Te, 550C, 60'	Te/Cu/Au	+1	7E-7	5E-6	7	0.21
21b	$CdCl_2$ only	Cu/Au	+1	6E-5	7E-3	120	0.39
21a	Ar, 550C, 60'+ $CdCl_2$	Cu/Au	+12	2E-3	2E-1	100	0.30
31a	Te, 550C, 60'+ $CdCl_2$	Cu/Au	+18	5E-4	4E-2	90	0.29

Comparing the two sets of data, the $CdCl_2$ treatment increases both dark and light conductivity by 3-4 orders of magnitude. Cell results obtained by $CdCl_2$ treatment by numerous groups over the past decade, suggested an increase in conductivity, but the measurements in Table 1 confirm the magnitude. All the CdTe films are photoconductive after treatment. The thermovoltage measurements of as-deposited CdTe films is slightly negative, which indicates intrinsic conductivity due to higher electron mobility compared to holes. All of the treated films show positive thermovoltage, indicating a shift to p-type conductivity. Both sets of data, with and without $CdCl_2$ treatment, show that the HTA increased the light conductivity more than the Te treatment; i.e., the light conductivity is about 10 times higher with the HTA. This was unexpected and is also true for both types of contacts. The effect on the activation energy is less clear, but a significant increase in conductivity with little change in E_a implies an increase in mobility. An increase in mobility of 3-5 orders of magnitude is huge, and signifies a change in transport mechanism. Further comparison is difficult since it is not clear whether to compare to the Au or the Te/Cu/Au data. We plan to pursue this further by repeating the sample fabrication and treatment using a single contact type and at different levels of moisture in the vapor ambient, which is expected to shift the chemical equilibrium to Te vacancy, inhibiting p-type conductivity.

VOLTAGE DEPENDENT PHOTOCURRENT COLLECTION

The July monthly report showed the effect of voltage dependent collection $J_L(V)$ in both J-V and QE data. Considerable effort has been spent in recent months to understand $J_L(V)$ in a wide range of CdTe devices. We have used the procedure described by Phillips [7] of measuring J-V at different intensities, including dark, and taking the

difference to quantify $J_L(V)$. Then we have fit this using a simple expression used to describe $J_L(V)$ effects in a-Si [8].

According to reference 7, measuring the J-V curves at different intensities, and plotting their difference normalized to the difference of the maximum current at farthest reverse bias yields the voltage dependence of the photocurrent collection $\eta_C(V)$. The equation for J-V at a given intensity 1 is

$$J_1 = J_0 \exp\left[\frac{q}{AkT}V'\right] + GV' - J_{L1}(V) \tag{1}$$
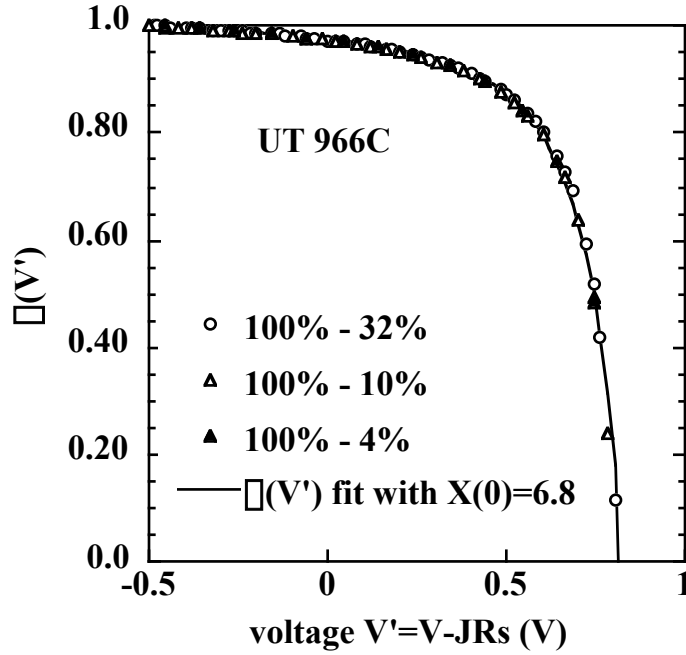
with

$$V' = V - RJ \tag{2}$$

and

$$J_{L1}(V') = J_{L01}\eta_C(V') \tag{3}$$

at each intensity. We neglect the GV term since we only analyze devices with relatively low dark shunts and at forward bias where GV is negligible compared to the diode current. J_{LO} in Equation 3 is the maximum photocurrent at reverse bias such that there are negligible collection losses and is proportional to light intensity. Then we calculate $\eta_C(V')$ as the difference of $J(V')$ at two intensities as

$$\eta_c(V') = \left[[J_1(V') - J_2(V')]/[J_{LO1} - J_{LO2}]\right] \tag{4}$$

Figure 4 shows this for a CdS/CdTe device UT 966C made at University of Toledo, which was measured at 4 intensities (100%, 32%, 10% and 4%). They all give the same voltage dependent collection function $\eta_C(V')$ when subtracted from the 100% data, and normalized by the difference in intensity. At maximum power, approximately 0.6V, the photocurrent has been reduced by about 25%. This indicates that $\eta_C(V')$ is clearly a major loss to FF.

Figure 4. Collection function $\eta_C(V')$ **for UT966C obtained using Equation 4 and data measured at 4 intensities. Also shown is fit to the 100%-10% data using Equation 5 with X(0)=6.8 and** V_{FB}**=0.813V.**

Analysis of voltage dependent collection in a-Si solar cells by many groups has shown that J-V and QE(V) data could be fit with the expression[8]:

$$\eta_c(V') = X\left[1 - \exp\left(X^{-1}\right)\right] \tag{5}$$

Under the assumption of a uniform electric field, it was shown that the parameter X can be defined as

$$X(V) = \frac{L_c(0)}{d}\left(1 - \frac{V}{V_{FB}}\right) \tag{6}$$

Here $L_C(0)$ is the collection drift length given by

$$L_c(0) = \mu\tau E(0) = \mu\tau\frac{V_{FB}}{d} \tag{7}$$

where V_{FB} is the flat band voltage which makes the field go to zero. The ratio $X(0)=L_C(0)/d$ was commonly used to characterize the voltage dependent collection in a-Si. This model, contained in Equations 5-7, was widely and successfully applied to a-Si p-i-n solar cells despite questions about the validity of the simplifying assumptions. Nonetheless, Figure 4 shows the excellent fit (regression coefficient of >0.99) to the data using Equation 5 and the parameters in the caption. It gives a single parameter $X(0)$, which can be used to characterize photocurrent collection losses in CdTe. The fit suggests the simple model for field dependent collection developed for a-Si has some applicability to understanding CdTe devices. This is reasonable since CdTe is nearly intrinsic like a-Si. Figure 5 shows $\eta_C(V')$ obtained using 100% and 10% intensity and the best fit using Equation 5 for a device from First Solar which had much thicker CdTe layer than the device in Figure 4. The difference between data and fit is also shown. Figures 4 and 5 show that Equation 5 applies to devices made by different methods and with different CdTe thickness. We have analyzed over 10 different CdTe devices from several sources of manufacture having FF from 55 to 70, and all show strong voltage dependence to the photocurrent with values of $X(0)$ from 6 to 20. The meaning of $X(0)$ is unclear at present. There are questions regarding assumption of a uniform field, neglect of diffusion, whether $X(0)$ represents hole or electron transport and whether d represents the entire CdTe thickness. This will be the subject of future effort using bifacial measurements, devices of varying thickness, and AMPS simulations. Subsequent work will correlate $X(0)$ with FF and will quantify the impact of $J_L(V)$ losses on FF.
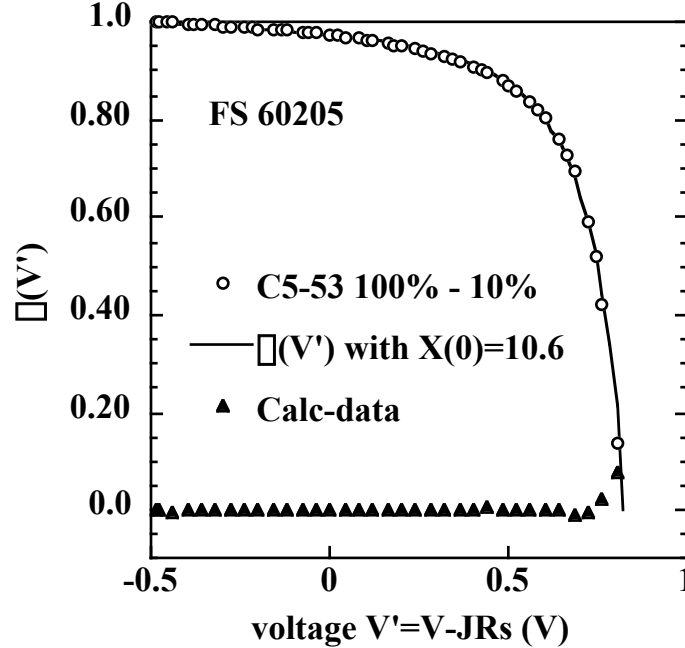

Figure 5. Collection function $\eta_C(V')$ for First Solar device from plate 60205 obtained using Equation 4 and fit using Equation 5 with X(0)=10.6 and V_{FB}=0.870 V. Difference between fit and data is shown.

TRANSPARENT BACK CONTACTS

Having a transparent CdTe contact will allow probing of the back contact using J-V and QE measurements. Our approach is to develop a Cu-doped ZnTe layer for the primary contact (to CdTe) and then apply an ITO layer for the secondary contact (current carrying). Two ZnTe solution growth processes have been developed, one based on sulfate and one on chloride chemistry.

ZnTe films were deposited electrochemically on TEC-15 SnO_2 for characterization. The chemical bath was an unstirred aqueous solution containing 0.1M $ZnSO_4$ for the sulfate bath or $ZnCl_2$ for the chloride bath and 0.001M TeO_2. The source of copper was a 0.001M $CuSO_4$ or $CuCl_2$, respectively. The electrochemical cell consisted of zinc anode in electrical contact with the substrate. To optimize the process, a series of deposition were carried out varying the temperature, the deposition time, and Cu concentration. Based on these results the baseline parameters were set as T~70C, time=10 mins and Cu concentration of 5E-5. The best films obtained had transmisson of ~ 70% and a sheet resistance of 7-9 ohms/sq. GIXRD measurements indicated the ZnTe films are ~50nm thick and have poorly nucleated small grain structure. Figure 7 shows T/(1-R) for glass/SnO_2 (Tec15) substrates for ZnTe by the two methods under conditions used for contacting devices reported here. The ZnTe has 30-60% transparency at the wavelengths of interest from 400-800 nm. Following the ZnTe layer primary contact growth on the FS CdS/CdTe substrate, a sputtered ITO layer with 20 Ω/sq and evaporated Ni/Al grids were deposited to complete the secondary contact. Devices were scribed with an area of 0.47 cm^2. Cells were tested initially then after heat treatments of 180°C in Ar for 10-30 minutes.
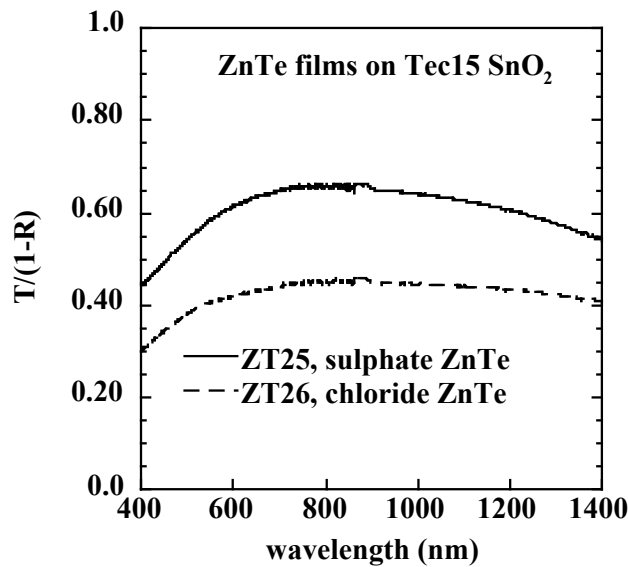

Figure 7. Transmission normalized by 1-R for ZnTe films on Tec15 produced by two different methods. These are same conditions as used for making devices.

We describe preliminary results from applying the two types of ZnTe layers. For this first experiment, the CdTe surface was not etched nor was a Te layer deposited, thus there was no Te layer on the surface. In future devices the influence of a Te layer is known to lead to better device results, which will be examined. However even the preliminary results are intriguing. Figure 8 shows the JV curves of a device made using FS CdS/CdTe and the ZnTe from the sulfate bath for illumination through the CdS and ZnTe. Table 2 shows the J-V performance. Performance was comparable between the sulfate and chloride chemistry. The low J_{SC} for illumination through the ZnTe is lower than expected considering the absorption of ZnTe but could be due to reflection losses.

Table 2. J-V performance for FS 222L4.6-4 for light through the CdS or the ZnTe. Values are average of the up and down traces shown in Figure 8.

Light through	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Eff. (%)	R_{OC} (Ω-cm^2)	Gsc (mS/cm^2)
CdS	0.655	14.3	49.6	5.1	8	5
ZnTe	0.622	2.8	66.4	1.2	21	0
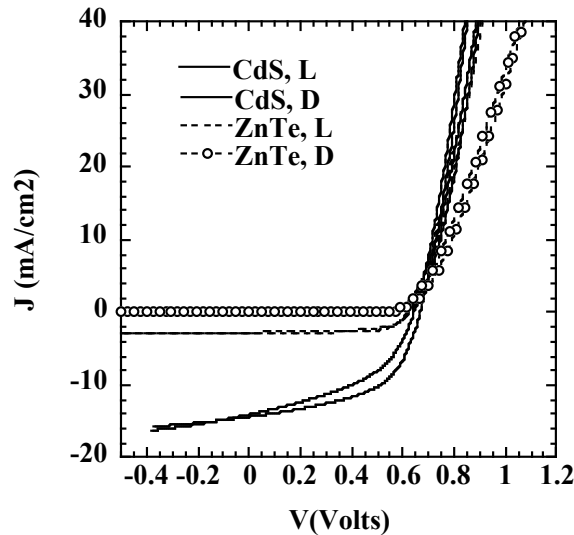
Figure 8. J-V curves from FS 222L4.6-4 for light through the CdS or the ZnTe.

The CdS/CdTe device is supposedly a n/p heterojunction with minority carrier photogenerated electrons in the CdTe drifting and diffusing to the CdS and majority carrier holes moving to the ZnTe contact. Given the high absorption coefficient, one would expect the collection hence FF to be higher for illumination through the CdS compared to light through the ZnTe. By analogy with a bifacial a-Si device [9] the FF is always higher for light through the p-layer compared to the n-layer since holes are the

limiting carrier. However, in both pieces of bifacial CdS/CdTe/ZnTe devices that we made, the FF is always higher for ZnTe illumination. The reason for the low FF for illumination through CdS is clearly seen to be increased voltage dependent current collection, as shown by different values of G_{SC} in Table 1. This is quite surprising and implies that the *hole* is the limiting carrier, i.e. minority carrier, in the CdTe not the electron was would be expected for a p-type material. Also note that the "dark" curve has higher resistance for illumination through CdS or ZnTe. One would expect them to be same since the device is in the dark in both cases. However, in our J-V measurement, the device is not placed totally in the dark. Room light is incident on the back. Since in most cases the opaque back contact blocks any room light this is not an issue, but with bifacial devices there can be some residual light. The entire piece will be covered for future dark measurements. Substantial evolution in the J-V curves occurred with heat treatment and will be investigated further in subsequent reports. Future work will include varying the surface treatment to create a Te layer and Cu doping of the ZnTe. Bifacial J-V-T, collection length, and QE measurements will be made when device performance improves.


HIGH THROUGHPUT CdTe DEPOSITION BY VAPOR TRANSPORT (VT)

Vapor transport deposited CdTe films are potentially sensitive to contamination from the source heating filament and surrounding manifold. This is because the filament and manifold must be at high temperature and are in contact with the source vapor. Sufficient temperature is required to radiatively couple the filament to the CdTe source material to generate the high partial pressure needed to saturate the source vapor. Furthermore, the source vapor will come into contact with the manifold wall as it moves towards the emergence slit. The effects of contamination on devices are not known but are expected to be reactor-specific. To systematically study the effects of source contamination, we have been planning to employ CdTe sources of known composition (impurity content) and then endeavor to correlate film composition and cell performance with these source materials. However, during this reporting period, a sharp decrease in device performance, from 11% to less than 7%, accompanied by severe shunting and hysteresis, was found and appears to be correlated with quantifiable filament degradation, which provides a different opportunity to study impurities.

In a filament-heated vapor generating source, such as that used at IEC, the selection of filament materials is based on the wire emissivity, which determines the radiative coupling to the CdTe source material, and the wire resistivity, which, together with the filament winding geometry, determine the electrical power needed for heating. In the IEC system, many metals, such as Ta, W, Ni-Cr and other alloys were originally considered. The alloy kanthal-A was selected, having the composition: 70% Fe, 20% Cr, 5% Al, and 1% Si. In anticipation of contamination by sublimation, a procedure was developed to form an oxide diffusion barrier on the wire surface prior to installation, by heating to ~600°C in air for 20 minutes.

The selection of manifold material was based on a combination of machinable characteristics, emissivity, and cost. Aremco machinable ceramic was selected, composed of oxides of Si and Al. Thermal calibration of the complete source generator showed that operation of the kanthal filament at ~1000°C translated to a CdTe source temperature of ~800°C and a manifold wall temperature of ~700°C. From this, we expected and found a small CdTe deposit accumulated on the manifold wall from run-to-run. Any contamination from the manifold would have to diffuse through this accumulating CdTe layer. Furthermore, measurements of the slit aperture showed no measurable change after 80 depositions, evidence of minimal direct contamination from the manifold.

Figure 9 shows the J-V behavior obtained before and after filament degradation, for devices from runs VT82 and VT85. Both are the –32 piece, from same plate location. Both devices had the same post-deposition processing (HTA, BDH etch plus 50Å Te, then Cu/Au contact). The figure shows that cells on VT85.32 exhibited more shunting, more hysteresis, lower V_{OC} and FF, and lower yield (1/8 vs 6/8) than VT82.32. Figure 10 shows data from VT86.12 and a piece from First Solar FS72435F2.11, which were co-processed at IEC, receiving the same $CdCl_2$, BDH, 50 nm Te, and Cu/Au contact. Clearly the FS device is well behaved with no shunting or hysteresis while the VT86 device is not well behaved. Since they had identical processing treatment, we concluded that the origin of the poor J-V characteristics was in the CdTe layer deposited in the IEC vapor transport system.
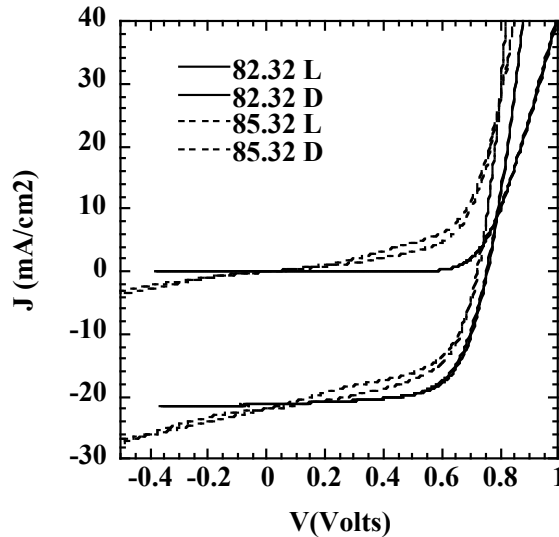
Figure 9. Light and dark J-V curves from two IEC VT pieces.
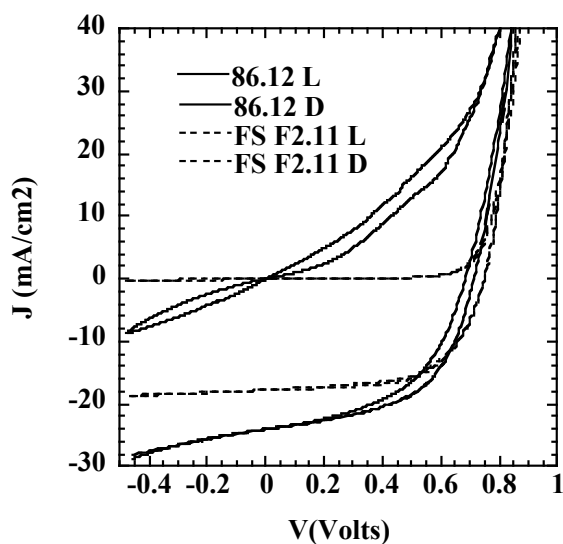
Figure 10. Light and dark J-V curves from an IEC VT piece and a FS piece, which were co-processed.

To determine the extent of chemical contamination, samples from depositions made prior to and after filament degradation and after filament replacement were analyzed by XRD, EDS and SIMS. Table 3 shows the deposition numbers and attributes for the vapor transport system. In the table, "new" CdTe charge indicates that the CdTe was replaced for each deposition. None indicates that no CdTe powder was placed in the source chamber. Any deposition obtained thus resulted from sublimation of previously deposited material from the manifold walls.

Table 3. Vapor transport deposition conditions.

Deposition	Filament	CdTe Charge
VT82	Old kanthal	New
VT85	Old kanthal	New
VT91	Old kanthal	New
VT95	New kanthal	New
VT96	New kanthal	None

XRD and EDS analysis were conducted on films samples from these and other runs. No differences were found in composition or diffraction patterns, indicating no gross compositional or structural effects due to presumed contaminants. EDS analysis was also conducted on the filament wire, removed after deposition VT91 due to visible scaling of the filament wire in some portions. At 30 kV, with a penetration depth exceeding 1 micron, no aluminum was detected in the wire, suggesting a loss. We also analyzed 3 pieces of new kanthal-A wire taken at 1 meter spacings along the wire spool and found

identical composition, with 5% Al. Finally, we had previously analyzed air-annealed wire and found similar composition, showing that the air anneal did not appreciably change the wire surface composition.

As-deposited film samples were further analyzed by Sally Asher at NREL using SIMS. The samples were glass/SnO_2 (Tec15)/Ga_2O_3/CdS/CdTe and received no $CdCl_2$ or contacting treatments. SIMS depth profiles were collected with a Cameca IMS-3F using high mass resolution for the profiles with the majority of the elements. The profiles containing Ga and In were performed under low mass resolution conditions since it is impossible to separate the isobaric species ^{113}Cd from ^{113}In, and ^{115}In from ^{115}Sn. All profiles were acquired using O_2^+ primary ions and detection of positive secondary ions. The data was collected from a circular area ~60 μm in diameter, in the center of a 150x150 μm^2 crater for ^{27}Al, ^{28}Si, ^{32}S, ^{35}Cl, ^{52}Cr, ^{56}Fe, ^{59}Co, ^{63}Cu, ^{111}Cd, ^{119}Sn and ^{125}Te.

The Cu levels in the CdTe were found to be high for un-contacted material, at roughly 10^{18} cm^{-3}, indicating an elevated base level, probably as a residual contaminant not removed during purification. All of the samples exhibited Si and Al contamination. The Si contaminant level was very high (~0.5 at %) in sample VT91, the last deposition with the old filament. There also appears to be significant Al contamination in the same sample, suggesting that visible filament scaling can transfer Al to the depositing film. The Si must originate in the source ampoule and/or the manifold. As the source ampoules exhibit no devitrification or erosion, we must assume that any Si originates in the manifold.

We are presently developing a more inert source to overcome filament and source degradation effects and to facilitate a systematic investigation of CdTe source purity and contaminants on the performance of CdTe cells.

CdTe TEAM ACTIVITY

The Institute has maintained a high level of collaboration with team members, in particular with First Solar. Towards the goal of developing vapor $CdCl_2$ treatments, IEC: prepared and submitted detailed reports on modeling $CdCl_2$ vapor delivery; constructed a new $CdCl_2$ source generator to carry out experiments with First Solar and IEC CdTe/CdS samples; is carrying out experiments to directly compare treatment in $CdCl_2$ vapor with treatment of $CdCl_2$-coated samples; and is investigating "source poisoning" issues associated with oxide formation in the source generator, which reduces the $CdCl_2$ gas phase concentration.   Towards the goal of back contact development, IEC has been characterizing the structure and composition of the back surface of First solar production plates and of newly developed contacts made by a third party company for First Solar. IEC has also been cooperating in the analysis of CdS film properties, CdTe-CdS interaction after processing, and CdS/TCO quality assurance issues for First Solar. Brian McCandless traveled to First Solar in September and made a presentation to the technical staff on quantifying the effects of post-deposition treatment, including the use of GIXRD,

contact wetting angle and correlating as-deposited CdS transmission to completed device quantum efficiency.

Collaboration with Canrom has also been on-going, with respect to post-deposition processing methods for Canrom CdTe/CdS and to the Team-related issue of evaluation of humidity during cell stress. This follow-up to the samples stressed in the dark at 85C at different humidities consist of repeating the stress conditions but in the light with the calls at V_{OC}. Cells for this round are being fabricated and results will be presented at the next team meeting.

Steve Hegedus traveled to First Solar in October to participate in a meeting of First Solar's Third Level Metrics Team. He presented new results from graduate student Darshini Desai on V_{OC} measurements at very low temperature, showing saturation of V_{OC} with intensity and temperature below 200K. Stressed and unstressed devices where characterized. The saturated V_{OC} at low temperature may be the built-in voltage and the V_{OC} extrapolated to 0K is approximately the CdTe bandgap, and both were somewhat correlated with room temperature V_{OC} before and after stress. Both parameters have potential to be fundamental metrics of the CdTe junction. Considerable work is needed in both experimental and modeling to identify the relation of these measurements to CdTe device operation. Results on voltage dependent current collection were also presented.

Recently, we received a set of 7 samples from First Solar, which had been cut from different modules. Baseline devices, as well as those having unusual J-V performance were selected. Complete analysis of J-V-T and QE(V) is in progress

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Sincerely,

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